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Luminescence of Silicon Nanocrystals and Porous Silicon

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Silicon nanocrystals have been made by a high temperature aerosol method. When passivated with 0.5-1 nm of oxide, the crystallites luminesce with ca. 5% quantum yield at room temperature, at visible wavelengths about 1 eV above the bulk silicon band gap. Spectroscopy shows that the nanocrystals behave as indirect gap semiconductors with phonon induced spectra. The quantum yield at room temperature is high, not because the nanocrystals are somewhat direct gap like, but because the fast radiationless processes which dominate carrier dynamics in bulk silicon are suppressed in nanocrystal silicon. The dynamics become molecule-like in nanocrystal silicon.

1. Introduction

Significant process has been made in understanding the detailed quantum mechanics of direct gap semiconductor nanocrystals, principally the II-VI material CdSe in the strong confinement limit, as evidenced by a number of talks given in this OPN '94 meeting. In these nanocrystals the lowest electronic (band gap) transition is strongly dipole allowed for all sizes.

In an indirect gap material such as silicon, luminescence is electric dipole forbidden by translational symmetry. In nanocrystals a purely electronic transition dipole should develop and increase as size decreases; in addition the vibronically induced TO phonon luminescence is predicted to become faster as size decreases[1,2]. Thus nanocrystal Si might be a useful luminescent material. Indeed, porous Si emits efficiently at room temperature[3,4], and this emission has been attributed to nanocrystals having faster radiative rates than bulk silicon. If a practical and fast(gigahertz)luminescent silicon material could be found, optical interconnections for VLSI silicon circuits would become feasible. This is an important goal for the computer/telecommunications industry. In this short article I discuss recent work in understanding this luminescence.

2. Synthesis, Characterization, and Optical Properties

Silicon nanocrystals are made in an aerosol apparatus that has two stages: an initial oven at 1000 C where flowing disilane is pyrolyzed to make Si nanocrystals. In a second oven, a brief high temperature oxidation creates a 0.5-0.8 nm oxide shell on each crystallite, to passivate the surface and to impart particle solubility in hydrogen bonding type solvents. The flowing aerosol is bubbled thought ethylene glycol, and a nanocrystal colloid forms[5].

X-ray powder diffraction and TEM show that the silicon core is a single crystal with lattice constant unchanged from the bulk at present resolution. Near edge X-ray absorption shows that the silicon:silicon dioxide interface is about a monolayer thick. Particles with 3 nm Si cores emit near 800nm; deep red 650 nm emission comes from particles between 1 and 2 nm in size[6].

The high temperature silicon nanocrystal method necessarily makes a moderately wide size distribution. Sizes can be partially separated using size exclusion chromatography, and precipitation methods. Figure 1 shows a rather broad nanocrystal distribution (A) that has been separated into two parts: (B) a narrow fraction of smaller particles, and (C) a broader fraction of larger
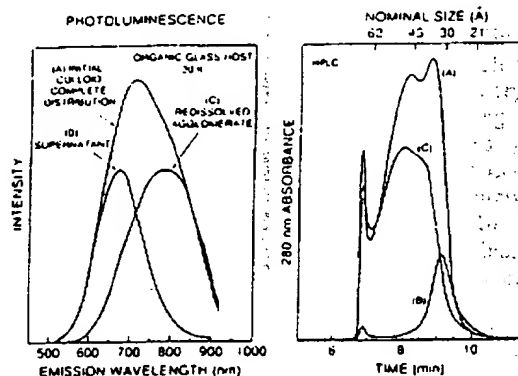

Fig. 1 (left-hand side) Spectrally corrected Si nanocrystal luminescence in organic glass (350nm excitation, 20K). (right-hand side) Corresponding liquid chromatograms with approximate logarithmic size calibration. Relative intensities are arbitrary. Adapted from ref. 7.

particles. (B) emits in the 600-700nm region, on the higher energy side of the broad, featureless emission of (A)[7].

If we "activate" (B) by 100 C heating with addition of acidic hydrogen peroxide, then room temperature photoluminescence is observed with quantum yields of about 5%. Activation appears to passivate the last few "dangling bonds" on the particle. The photoluminescence quantum yields are measured in optically thin, clear solutions, and are referenced against the known quantum yields of organic dyes. At low temperature, the quantum yield increases to near 50%. However, the lifetimes are quite long: near 50 microseconds at room temperature, increasing to several milliseconds at liquid He temperatures[7].

The emission (B) is still broadened by a residual size distribution. The photoluminescence excitation spectrum on the high energy side, at 630 nm, records the excitation spectrum of the smallest crystallites in the distribution. This spectrum in Figure 3 shows indirect gap type absorption extrapolating to a near 630 nm band gap. This continuous spectrum is quite different than in CdSe nanocrystals where discrete transitions are observed in absorption. In CdSe only those few discrete transitions strongly allowed under electron dipole selection rules are observed. In effect the spectrum is simplified. In Si nanocrystals, it would seem that all possible transitions are present, at roughly equal intensities due to phonon coupling, yielding a dense, apparently continuous optical absorption.
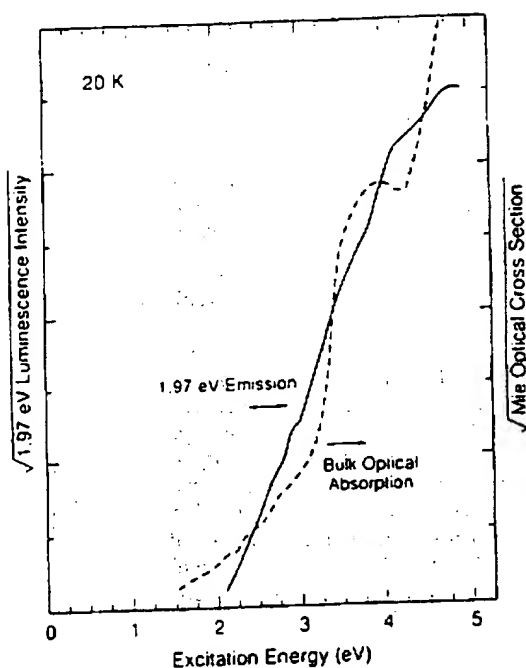
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Fig. 2 Normalized luminescence Excitation Spectra of Si nanocrystal emission at 630 nm, adapted from ref. 7.
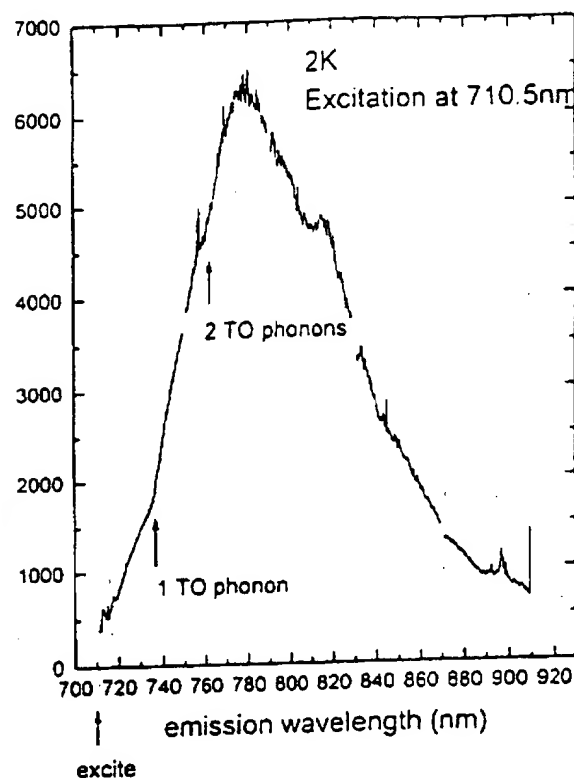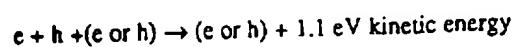

Fig. 3 Luminescence observed from 710.5 nm cw laser excitation in organic glass at 2 K. TO phonon thresholds are marked.

Figure 2 also shows no structure in the region of the Si ultraviolet direct gap above 3.4 eV. It would appear that the Si direct gap broadens, rather than shifts to higher energy as in CdSe. This may reflect the fact that the Si gap at 3.4 eV is actually a saddle point in the Brillouin zone.

Figure 3 shows the luminescence spectrum observed following laser excitation at 710 nm, corresponding to resonant excitation of only larger nanocrystals in the size distribution. This emission shows steps due to TO phonon thresholds. These resonant spectra are quite similar to those observed and analyzed in porous Si luminescence[8,9,10]. This spectrum, along with the excitation spectrum and the very long measured lifetimes, prove that the Si nanocrystals emitting near 2.0 eV are indirect gap type, with TO phonon (indirect) luminescence dominating purely electronic (direct) luminescence, in agreement with recent theory[2].

3. Comparison of Nanocrystal and Bulk Crystalline Silicon

The Si nanocrystal data are quite similar to the porous silicon data, and I believe that the two systems have a common mechanism. The chromophore is a passivated Si nanocrystal with a band gap larger than the bulk band gap due to three dimensional quantum confinement.

As we measure both the quantum yield of emission and the lifetime τ we can obtain both the radiative rate Γ_r and the nonradiative rate Γ_{nr} such that $\tau^{-1}=\Gamma_r+\Gamma_{nr}$. Experimentally, Γ_r has a maximum value of 2×10^3 s^{-1} at

100K. By comparison, in crystalline Si the free exciton, bound by Coulomb forces at low temperature, has a phonon induced radiative rate of 2×10^4 s^{-1} [11,12]. Thus, the radiative rate of the nanocrystal is not faster than that of bulk Si.

Actually, the luminescence efficiency of bulk crystalline Si and nanocrystal Si can both be high at liquid He temperatures. In the bulk crystal, an exciton typically trapped at a shallow defect, or at a foreign atom, luminesces with high quantum yield and long lifetime, in analogy with an exciton "trapped" inside a nanocrystal. In both cases a partially superimposed electron and hole emit slowly with TO phonon participation. In both cases nonradiative relaxation producing lattice heat is relatively unimportant in the trapped pair.

The major difference occurs in the room temperature kinetics. In nanocrystals, confinement within one crystallite keeps the electron-hole pair superimposed, and luminescence occurs at room temperature as well. However, in the bulk crystal the exciton Coulomb binding energy is less than kT at room temperature, and the electron hole pair separates. If the crystal contains even relatively rare deep defects that catalyze non radiative recombination, then the mobile carriers will find and trap in such centers. If such deep traps are not present, then free carriers can live for milliseconds at very low density. However, at moderate densities the lifetime shortens due to three body Auger recombination[13]

$$e + h + (e \text{ or } h) \rightarrow (e \text{ or } h) + 1.1 \text{ eV kinetic energy}$$

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As a result of both processes, the quantum yield of luminescence is negligible at room temperature in bulk silicon.

Both bulk nonradiative mechanisms are severely decreased in nanocrystals as carriers become stationary. First, the Auger process is much less important as pairs in separate crystallites are electrically isolated and do not interact[14]. (As the optical absorption cross section scales with nanocrystal volume, the probability of two pairs existing in one crystallite decreases for small crystallites at constant excitation intensity.) Second, the effect of rare deep defects is lessened by the fact that one defect can quench luminescence from just one nanocrystal. In the bulk crystal, one defect can quench luminescence from a much larger volume due to the carrier mobility. If surface passivation does not introduce new deep traps, then luminescence increases in nanocrystals.

In this model, the factors that cause photoluminescence to increase also decrease electrical conductivity in nanocrystal films such as porous Si. If a nanocrystal shows quantum size effects in its optical spectra, then there must be a barrier to electron motion between crystallites.

Nevertheless, if the pores in the nanocrystal film contain liquid electrolyte, as in liquid junction porous Si electroluminescent diodes, then the film Fermi level can be adjusted via the electrolyte redox potential[15]. Slow, hopping conductivity occurs in such films, as well as carrier motion in the electrolyte. These devices show novel physics and merit further research.

the vibrations of a finite lattice, in the nanocrystal. As shown in Figure 4, for some time it has been understood that several size regimes exist in semiconductor optical spectroscopy: (a) molecular, (b) nanocrystal, or quantum dot, (c) polariton, and (d) macroscopic crystal[16]. Silicon demonstrates that interesting size regimes exist in carrier dynamics as well. This aspect is not yet completely understood.

Acknowledgement

References

1) T. Takagahara, K. Takeda: Phys. Rev. B 46(1992) 15587.

2) M. S. Hybertsen: Phys. Rev. Lett. 72(1994) 1514.

3) L. T. Canham: Appl. Phys. Lett. 57(1990) 1046.

4) N. Koshida, H. Koyama: Jpn. J. Appl. Phys. 30(1991) L1221.

5) K. A. Littau, P. J. Szajowski, P. J. Muller, A. J. Kortan, L. E. Brus: J. Phys. Chem. 97(1993) 1224.

6) S. Schuppler, S. L. Friedman, M. A. Marcus, D. L. Adler, Y.-H. Xie, F. M. Ross, T. D. Harris, W. L. Brown, Y. J. Chabal, L. E. Brus, P. H. Citrin: Phys. Rev. Lett. 72(1994) 2648.

7) W. L. Wilson, P. J. Szajowski, L. E. Brus: Science 262(1993) 1242.

8) P. D. Calcott, K. J. Nash, L. T. Canham, M. J. Kane, D. J. Brumhead: J. Phys.: Condens. Matter 5(1993) L91.

9) P. D. Calcott, K. J. Nash, L. T. Canham, M. J. Kane, D. J. Brumhead: J. Lumin. 57(1993) 257.

10) T. Suemoto, K. Tanaka, A. Nakajima: J. Phys. Soc. Jpn. 63(1994) Suppl. B 190.

11) J. R. Haynes, M. Lax, W. F. Flood: Prof. Int. Conf. Semicond. Phys. Prague 1961 p. 423.

12) J. D. Cuthbert: Phys. Rev. B 1(1970) 1552.

13) E. Yablonovitch, D. L. Allara, C. C. Chang, T. Gmitter, T. B. Bright: Phys. Rev. Lett. 57(1986) 249.

14) L. Brus, J. Phys. Chem. 98(1994) 3575.

15) A. Bsiesy, F. Muller, M. Ligeon, F. Gaspard, R. Herino, R. Romenstain, J. C. Vial: Phys. Rev. Lett. 71(1993) 637.
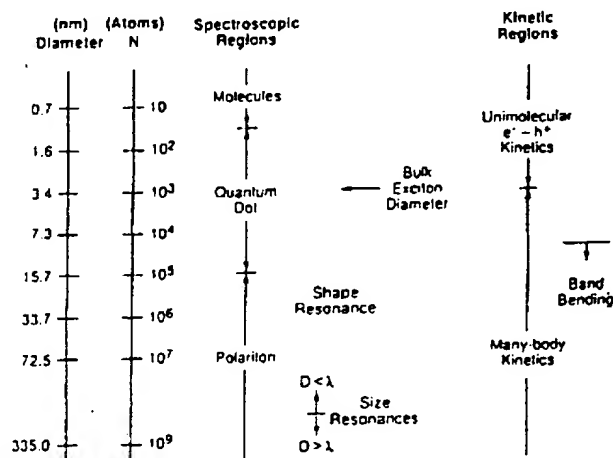
16) L. Brus, J. Phys. Chem. 90(1986) 2555.

Fig. 4 Schematic of Size Regimes for Semiconductor Crystallites.

4. Nanocrystal Size Regimes

This discussion shows how the electron-hole recombination kinetics transforms from molecule-like in nanocrystals, to the many interacting carrier kinetics of the macroscopic crystal. Molecule-like means that a partially superimposed electron and hole interact with each other directly via Coulomb and exchange forces, and with

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Commissioner for Patents

Sara W. Crane
Primary Examiner
Art Unit: 2811

The reply filed on 11 April 2005 and 3 January 2005 is not fully responsive to the prior Office Action because of the following omission(s) or matter(s):

The examiner could not find the third reference listed on the 1449 form of 11 April 2005 (Brus, L. "Luminescence of Silicon Nanocrystals and Porous Silicon," Japanese Journal of Applied Physics). There are only three prior art documents of this date in the scanned image file, the first two documents on the 1449 form, and a PCT search report. (And the missing document is listed as an "X" reference on the search report.)

Applicant is requested to supply another copy of the reference.

See 37 CFR 1.111. Since the above-mentioned reply appears to be *bona fide*, applicant is given **ONE (1) MONTH or THIRTY (30) DAYS** from the mailing date of this notice, whichever is longer, within which to supply the omission or correction in order to avoid abandonment. EXTENSIONS OF THIS TIME PERIOD MAY BE GRANTED UNDER 37 CFR 1.136(a).

Any inquiry concerning this communication or earlier communications from the examiner should be directed to S. Crane, whose telephone number is (571) 272-1652.

The supervisor for Art Unit 2811, Eddie Lee can be reached on (571) 272-1732. The fax phone number for the organization where this application or proceeding is assigned is 703-872-9306.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

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